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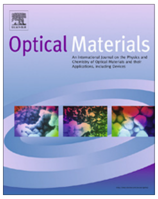

Alkaline aluminum phosphate glasses for thermal ion-exchanged optical waveguide

Fei Wang [a], Baojie Chen [b], Edwin Yue Bun Pun [b], Hai Lin [a,b,*]

[a] School of Textile and Material Engineering, Dalian Polytechnic University, Dalian 116034, China
[b] Department of Electronic Engineering, City University of Hong Kong, Kowloon, Hong Kong, China

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ABSTRACT

Alkaline aluminum phosphate glasses (NMAP) with excellent chemical durability for thermal ion-exchanged optical waveguide have been designed and investigated. The transition temperature Tg (470 °C) is higher than the ion-exchange temperature (390 °C), which is favorable to sustain the stability of the glass structure for planar waveguide fabrication. The effective diffusion coefficient D_e of K^+–Na^+ ion exchange in NMAP glasses is 0.110 μm^2/min, indicating that ion exchange can be achieved efficiently in the optical glasses. Single-mode channel waveguide has been fabricated on Er^{3+}/Yb^{3+} doped NMAP glass substrate by standard micro-fabrication and K^+–Na^+ ion exchange. The mode field diameter is 9.6 μm in the horizontal direction and 6.0 μm in the vertical direction, respectively, indicating an excellent overlap with a standard single-mode fiber. Judd–Ofelt intensity parameter Ω_2 is 5.47×10^{-20} cm^2, implying a strong asymmetrical and covalent environment around Er^{3+} in the optical glasses. The full width at half maximum and maximum stimulated emission cross section of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ are 30 nm and 6.80×10^{-21} cm^2, respectively, demonstrating that the phosphate glasses are potential glass candidates in developing compact optoelectronic devices. Pr^{3+}, Tm^{3+} and Ho^{3+} doped NMAP glasses are promising candidates to fabricate waveguide amplifiers and lasers operating at special telecommunication windows.

1. Introduction

In the past decades, optical waveguides have raised great interest as they are the most fundamental and integral part of integrated optics circuits. Glasses based integrated optical devices have several obvious advantages over other technologies such as low intrinsic absorption in the near infrared region of the spectrum, minimized coupling losses to optical fibers, and no intrinsic material birefringence compared to crystalline semiconductors [1–3]. Phosphate glasses are regarded as excellent glass host for waveguide laser fabrication mainly because of high solubility of rare-earth ions compared with other oxide glasses, which allows for high doping concentrations without significant lifetime reduction, resulting in high gain in short waveguides or cavities and a desirable feature in single-frequency lasers [4–6]. High-performance waveguide amplifiers or lasers have been fabricated in various earth-ion doped phosphate glasses [7–9] and commercial phosphate glasses such as Kigre Q89 [10] and Schott-IOG 1 [11].

Ion exchange has been widely used to fabricate low-loss glass waveguide due to various benefits compared with other fabrication techniques such as chemical vapor deposition, flame hydrolysis deposition, sol–gel deposition, optical writing and ion/proton beam implantation [12–14]. These benefits include high reliability, massive production, easy fabrication of single-mode waveguide, excellent mode matching to single-mode fiber through waveguide burial and low birefringence across a broad range of waveguide widths [1,7,15]. K^+–Na^+ ion exchange is one of most employed techniques to fabricate single-mode device, which is mainly attributed to the facts that the index change with pure KNO_3 melt is highly compatible with single-mode fibers, no concentration control of the melt is required and no subsequent metallic ion clusters are formed [16–18].

In this work, alkaline aluminum phosphate glasses (NMAP) with excellent chemical durability for thermal ion-exchanged optical waveguide have been designed and investigated. Single-mode glass channel waveguide has been fabricated on Er^{3+}/Yb^{3+} doped NMAP glass substrate by standard micro-fabrication process and K^+–Na^+ ion exchange. The effective diffusion coefficient D_e of K^+–Na^+ ion exchange in NMAP glasses has been deduced. The surface morphologies and the mode field diameters of the channel waveg-

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* Corresponding author at: School of Textile and Material Engineering, Dalian Polytechnic University, Dalian 116034, China. Tel.: +86 411 86323097.
E-mail address: lhai8686@yahoo.com (H. Lin).

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uide have been characterized. Judd–Ofelt intensity parameter Ω_2 indicates a strong asymmetrical and covalent environment around Er^{3+} in the optical glasses. The full width at half maximum and maximum stimulated emission cross section of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ were derived to be 30 nm and 6.80×10^{-21} cm^2, respectively. This work demonstrates that NMAP glasses possess great potential for developing rare-earth ions doped optical waveguide devices.

2. Experimental

2.1. Preparation and measurements of NMAP glasses

NMAP glasses were prepared from high-purity $NaPO_3$, $Mg(PO_3)_2$, Al_2O_3 and $Al(PO_3)_3$ powders according to the molar composition 67:4:4:25. Additional 2.0 wt% Er_2O_3 and 4.0 wt% Yb_2O_3 were introduced into NMAP glass composition to prepare active glass substrates for subsequent planar waveguide fabrication. Firstly, the well-mixed powders were preheated in a pure Pt crucible at 360 °C for 10 h to remove moisture, then melted at 1350 °C for 1 h, and finally quenched in a preheated aluminum mold. The obtained glasses were annealed at 470 °C for 3 h and then cooled down slowly to room temperature. For optical measurements, the annealed glasses were sliced and polished into pieces with parallel sides.

The density ρ was measured to be 2.720 g cm^{-3} with the Archimedes method. The number densities of Er^{3+} and Yb^{3+} were calculated to be 1.616×10^{20} cm^3 and 3.137×10^{20} cm^3, respectively. The refractive indices were determined to be 1.5182 at 632.8 nm and 1.5042 at 1536 nm, respectively, using a Metricon 2010 prism coupler. At all other wavelengths, the refractive indices can be derived by the Cauchy equation $n = A + B/\lambda^2$ [19] with $A = 1.5013$ and $B = 6752$ nm^2 deduced from the refractive indices at 632.8 and 1536 nm. Differential thermal analysis scan was carried out by a WCR-2D differential thermal analyzer at a rate of 10 °C/min from room temperature to 700 °C. Absorption spectrum in UV/VIS/NIR regions was recorded with a Perkin-Elmer Lambda 19 double-beam spectrophotometer. Infrared fluorescence spectrum was determined by a Jobin Yvon Fluorolog-3 spectrophotometer equipped with a NIR PMT detector adopting a commercial CW Xe-lamp as excitation source. Fluorescence decay curve was recorded under the same setup using a flash Xe-lamp.

2.2. Fabrication and characterization of planar waveguide

Before preparing K^+–Na^+ ion-exchanged waveguide, Er^{3+}/Yb^{3+} co-doped NMAP glass substrates were optically polished and cleaned. Slab waveguide was fabricated by a thermal ion-exchange process at 390 °C for 2 h with pure molten KNO_3. A 150 nm thick high-quality aluminum film was deposited on the glass surface using an Edwards Auto 306 thermal evaporator, and then ion-exchanged channels were opened by standard microfabrication process and wet chemical etching method with a 4 μm mask. The ion-exchange process for channel waveguide fabrication was performed in a molten bath of pure KNO_3 at 390 °C for 1 h. After cooling down to room temperature, the aluminum film was removed from the waveguide surface and two end-faces were polished for further optical measurement. The refractive index profiles of the slab waveguide were measured by a Metricon 2010 prism coupler. The surfaces of the ion-exchanged channel waveguide were investigated using an atomic force microscope. 1.55 μm laser light was coupled into the channel waveguide, and the near-field mode pattern at the output facet was examined using a video camera.

3. Results and discussion

Metaphosphates such as $NaPO_3$, $Mg(PO_3)_2$ and $Al(PO_3)_3$ are selected as raw materials because they exhibit low moisture and excellent glass forming ability in the family of phosphates. A proper content of Na_2O should be introduced into the glass host to achieve an effective ion exchange and a reasonable melt temperature. Na_2O act as glass modifiers in glass system and a high Na_2O concentration will result in poor chemical durability [20]. However, the glass host must be acid-resistant to open channels with the etching acid and be able to sustain a good surface quality in molten KNO_3 for hours to accomplish the ion-exchange process. Therefore, good chemical durability is a critical requirement for the glass host. Richard reported that the chemical durability of Na_2O–Al_2O_3–P_2O_5 glass system will improve with the increase of Al_2O_3 content as well as the decrease of Na_2O content and Al^{3+} ions can strengthen the glass network by cross-linking phosphate chains [21,22]. The additions of MgO and Al_2O_3 can achieve an improvement in the chemical durability, a decrease in the thermal expansion coefficient and an increase in the stabilization of the glass structure [23,24]. Beside the content of Al_2O_3 being introduced from $Al(PO_3)_3$, an additional low content of pure Al_2O_3 are added into NMAP glass composition to further improve the chemical stability. Table 1 lists basic property parameters of several ion-exchangeable phosphate glasses [25,26]. The density and transition temperature of NMAP glasses are measured to be 2.72 g cm^{-3} and 470 °C respectively, which are similar to the values of Schott IOG-1. The Abbe number V_d, $V_d = (n_d - 1)/(n_f - n_c)$, is used to reflect the dispersion of optical materials in relation to the refractive index. The refractive indices of the glass at 486.3 nm (n_f), 589.3 nm (n_d) and 656.3 nm (n_c) are solved by Cauchy equation $n = A + B/\lambda^2$ with $A = 1.5013$ and $B = 6752$ nm^2, and V_d of the doped glass is derived to be 40.4. Although the V_d is derived from the fitting refractive indices, which contains the possible deviation compared with the actual case, it still indicates that the dispersion in phosphate glasses can be reduced by optimizing the glass composition to some extent.

Fig. 1 shows the ternary phase diagram of Na_2O–Al_2O_3–P_2O_5 glass system obtained from Ref. [27]. Kishioka and Hayashi et al. noted that most of Al^{3+} ions in the glass system are 6-fold coordinated with a higher P_2O_5 content (P/O = 0.33) whereas those with a lower P_2O_5 content (P/O $\leqslant$ 0.25) are 4-fold coordinated, suggested by the existence of two peaks in the glass phase [27]. The molar composition of NMAP glasses in oxide form is $26.0Na_2O$–$3.1MgO$–$12.8Al_2O_3$–$58.1P_2O_5$. Generally, Mg^{2+} ions act as glass network modifiers to meet charge balance in NMAP glasses. The main molar composition of NMAP glasses is $26.8Na_2O$–$13.2Al_2O_3$–$60.0P_2O_5$. The coordinate of NMAP glass composition located within the peak of a higher P_2O_5 content indicates that most of the Al^{3+} ions in NMAP glasses are 6-fold coordinated.

Fig. 2(a) presents differential thermal analysis curve of NMAP glasses. The transition temperature Tg was derived to be 470 °C and is larger than the ion-exchange temperature (390 °C), which is favorable to sustain the stability of the glass structure for planar waveguide fabrication. No obvious crystallization peak has been

Table 1
Basic property parameters of various ion-exchangeable phosphate glasses.

Phosphate glasses	ρ (g cm^{-3})	n_d	V_d	Tg (°C)	Ref.
Schott IOG-1	2.74	1.523	67.5	474	–
WM-1	2.83	1.535	67.0	530	[25]
MM-1	3.20	1.567	48.6[a]	500	[26]
NMAP	2.72	1.521[a]	40.4[a]	470	This work

[a] Values are deduced by Cauchy equation.